

STUDIES OF DISPERSED MoS₂ CATALYSTS FOR COAL LIQUEFACTION

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INTRODUCTION

Dispersed MoS₂ catalysts are widely used to promote the direct liquefaction of coal. Studies of the structure and activity of these catalysts have been conducted to obtain a better understanding of their function in the conversion of coal and similar feedstocks. Two approaches were used. First, the technique of exfoliation/restacking was used to generate MoS₂ catalysts of varying physical structures. These catalysts were then characterized by physical and chemical analysis and by simple activity tests. In the second approach, a kinetic study of the competitive reactions among members of a set of compounds was made to establish the activity and selectivity profile of a highly dispersed MoS₂ catalyst derived from Mo(CO)₆.

EXPERIMENTAL

The preparation of the exfoliated/restacked catalysts has been described.^{1,2} In brief, a commercial sample of highly crystalline MoS₂ was intercalated by reaction with butyllithium in hexane. The lithium intercalated MoS₂ was recovered by filtration. Exfoliation was achieved by mixing the dry powder with water using ultrasonic radiation to assist dispersion. A suspension of finely divided exfoliated MoS₂ was formed that eventually flocculated on standing. The restacked material was recovered by filtration. To prepare MoS₂ intercalated with cobalt, the exfoliation step was accomplished by adding LiMoS₂ to an equivalent amount of Co(NO₃)₂ in an aqueous solution.

Catalyst activity tests were conducted using microautoclaves. The autoclaves were charged with Hondo resid (C = 81.9%, H = 10.6%, S = 5.1%, N = 0.9%, 20% distilled below 934° F), and 10 wt%

MoS₂ catalyst, pressurized with 1000 psig hydrogen and heated to 425 °C. The reactor was held at temperature for 60 minutes, then cooled. Conversion was determined by extraction with heptane, and the catalyst was further extracted with tetrahydrofuran before characterization.

The crystallite size and the crystal lattice parameters of the catalysts were obtained by X-ray diffraction.

Catalysts were also characterized by the controlled atmosphere programmed temperature oxidation (CAPTO) technique.³ This technique provides quantitative analyses for carbon, hydrogen, and sulfur. It also provides a record of the evolution of the oxidation products, CO₂, H₂O, and SO₂, as a function of oxidation temperature. These records may be interpreted in terms of the chemical species with which each of the elements is associated. For example, the aliphatic and aromatic forms of carbon in coal are readily discerned and measured.⁴

Activity and selectivity tests of dispersed MoS₂ catalysts were conducted using a set of six microautoclaves. Activity was determined by observing the extent of reduction of a series of pure compounds. The tests was performed in a double cycle. In the first cycle, the catalyst was prepared by the decomposition of Mo(CO)₆ in dodecane under a mixture of hydrogen and H₂S. The hydrogen sulfide was prepared *in situ* by addition of elemental sulfur. The reaction conditions were 385 °C for 60 minutes. This method has been shown to produce a coal conversion catalyst of very high activity.⁵ After the catalyst was formed, the microautoclaves were depressurized and the pure compound(s) to be reduced was added. Elemental sulfur was again added to maintain the degree of catalyst sulfidation constant. The microautoclave was again pressurized with 1000 psig hydrogen, and the test cycle run at the desired temperature (300-350 °C) for 60 minutes. The time record of the temperature and pressure within each of the six reactors was acquired on a diskette. The liquid products were recovered for analysis by GC/MS. The recovered catalysts were analyzed by X-ray diffraction.

RESULTS AND DISCUSSION

EFFECT OF COBALT ON THE STRUCTURE OF MoS₂ CATALYST.

The physical structure of a series of dispersed MoS₂ catalysts was manipulated through a series of experiments. The original sample of MoS₂ was modified by use of the exfoliation/restacking technique, which also allowed the incorporation of cobalt or other ions as promoters. The structural changes were followed by use of XRD. The original sample produced sharp peaks characteristic of a highly crystalline MoS₂. In contrast, the MoS₂ recovered after exfoliation/restacking produced broad peaks characteristic of a turbostratic structure. In addition, a pronounced reduction in stacking height of the crystallites was determined by measurement of the width at half-height of the 002 line. The average crystallite stacking dimension for the starting material was 375 Å. For the exfoliated/restacked material it was reduced to 185 Å.

When the exfoliation/restacking step was conducted using an aqueous solution of $\text{Co}(\text{NO}_3)_2$, the recovered material was profoundly changed. The XRD pattern contained a major peak with an interlayer spacing of $\sim 11.5 \text{ \AA}$ rather than the 6.14 \AA usually found for MoS_2 . Elemental analysis gave a Co/Mo atomic ratio of 0.61. The nitrogen content was essentially zero. These results support an intercalated structure with cobalt ion trapped between MoS_2 layers, probably as the hydroxide. The stacking height was estimated from the width of the 002 peak to be 110 \AA . Introduction of Co into the MoS_2 structure by this process provides a mixture of the metallic elements in the most intimate way possible.

Activity tests of the Co promoted catalyst confirmed that it was highly active in the hydrotreatment of Hondo resid.² The sulfur content of the recovered resid was reduced from 5.1% for the original material to 3.3% using exfoliated/restacked MoS_2 and to 2.6% using the cobalt promoted exfoliated/restacked MoS_2 .

A remarkable and unexpected change in the morphology of the Co-promoted material occurred under the hydrotreating conditions. The XRD of the recovered catalyst contained only one 002 peak for an interlayer spacing of 6.2 \AA . Thus, the intercalated cobalt ions were removed from between the layers of MoS_2 . The rest of the diffractogram was also profoundly changed. The rather broad peaks were replaced by narrow lines, indicating that the turbostratic structure of the original catalyst has been replaced by a highly crystalline structure. The stacking height was estimated to be $\sim 1000 \text{ \AA}$. Comparison of the original and recovered catalyst demonstrates that a brief period under moderate hydrotreating conditions was sufficient to induce a remarkable growth in crystallinity. Intercalation with Co was necessary to the annealing process because the catalyst from simple exfoliation/restacking was recovered virtually unchanged in its degree of crystallinity. Whether promotion of the development of crystallinity is due to cobalt's inherent ability to stabilize the edges of the MoS_2 crystal or due to its original placement between the layers is not presently known.

ANALYSIS OF MoS_2 BY CAPTO

The MoS_2 catalysts were analyzed by the CAPTO method to determine whether the observed differences in physical structure would be reflected in the temperature profiles of the sulfur response. The sulfur profiles result from the ramped temperature program applied as the sample is heated in a stream of oxygen. Previous work has related the temperature of evolution of SO_2 to the nature of the chemical species of sulfur bound in coal and coal minerals.^{3,4} For a complex mixture, patterns of sulfur response provide fingerprints related to the type and amount of the individual species. The sulfur profile for the starting material, highly crystalline MoS_2 , was dominated by a peak centered around 523°C (65.7%). Several smaller peaks were also resolved at lower temperatures (300°C , 2.8%; 383°C , 3.0%; 440°C , 28.5%). The profile for the exfoliated/restacked MoS_2 showed a marked shift to lower temperatures compared to the starting material. This profile was dominated by a peak at 434°C (76.5%), with smaller peaks at: 243°C , 2.1%; 299°C , 2.3%; 370°C , 15.4%, and a small high temperature peak at 619°C (3.7%). Because the exfoliation/restacking procedure does not alter the chemical state of the sulfur but only reconstructs the original crystallites in a new

pattern, the differences between the two profiles shows that the sulfur response is quite sensitive to the physical structure of the catalyst.

Recovered catalysts were also examined to determine the effects of exposure to hydrotreating conditions. The sulfur profile of the exfoliated/restacked catalyst after hydrotreatment with Hondo resid is much closer to that of the starting catalyst than to the original highly crystalline MoS₂. The major peak at 434 °C has grown and the two small peaks at lower temperatures coalesced. Only three peaks (289 °C, 9.1%; 381 °C, 2.0%; 434 °C, 86.3%) were necessary to fit the data instead of the four required by the starting material.

The sulfur evolution profiles of the Co intercalated MoS₂ is more complex than the exfoliated/restacked sample prepared without Co, but there are some similarities. The majority of the sulfur in both evolves at lower temperatures than the highly crystalline starting material and the two major peaks (370-390 °C and 435 °C) of both samples appear to be similar. In addition to these, the Co-intercalated sample has major peaks at 475 and 535 °C. The major disruption in crystalline structure caused by intercalation of cobalt has apparently stabilized a portion of the sulfur bound to molybdenum toward oxidation.

The CAPTO profile of the Co/MoS₂ catalyst recovered after being used in hydrotreatment is interesting in light of the high degree of crystallinity that was reflected by its XRD pattern. This is also complex and shows new features, as might be expected because new cobalt sulfide phases are formed during the hydrotreatment reaction. Two significant new peaks appear, one at a relatively low temperature, 317 °C, and one at 508 °C. The peaks centered around 437 and 629 °C have disappeared. In addition, the area under the peak centered about 535 °C has grown. The metamorphosis from intercalated MoS₂ to completely sulfided CoMo redistributed the sulfur. Some of the new forms are more readily oxidized and some are more difficult. This complex redistribution may be the result of the formation of cobalt sulfides combined with the sintering of crystallites to form a more highly stacked MoS₂.

Taken together, the various responses shown by the samples of differing physical and chemical structure indicate that CAPTO is a promising way of analyzing sulfided catalysts. It is conceivable that a quantitative means to determine the changes in crystallinity of catalysts as a function of time on-stream could be developed. In addition to the sulfur analyses described here, important information on the amount and character of coke deposits associated with dispersed catalyst prepared and used under various hydrotreating conditions has been obtained.

COMPETITIVE INHIBITION OF MoS₂

Earlier work at FETC has shown that dispersed and supported catalysts are poisoned and inhibited by exposure to even minor amounts of coal under liquefaction conditions.^{6,7} To determine more about the root causes of this repression of activity, a series of microautoclave experiments was made to investigate the inhibition of the hydrogenation function of a dispersed MoS₂ catalyst. As explained

in the experimental section, testing was performed in a two-cycle sequence of catalyst preparation followed by the hydrogenation reaction. In the first cycle, the MoS_2 catalyst was prepared fresh for each test by the decomposition of Mo(CO)_6 in dodecane under $\text{H}_2/\text{H}_2\text{S}$. In the second cycle, the hydrogenation reaction was conducted by adding naphthalene, which was selected as the reference compound for the hydrogenation reaction, and/or a compound from the family comprising biphenyl, fluorene, dibenzothiophene, dibenzofuran, and carbazole. Competition experiments were made by using two component mixtures of these compounds.

In the absence of competition, the hydrogenation of naphthalene went smoothly under hydrogen pressure of 2000 psi. The temperature and catalyst loading were adjusted so that the rate of the reaction to form tetralin could be readily measured. Only a minor amount of the further reduction of tetralin to decalin was observed at 300 °C. In this case, it was possible to follow the kinetics of the reaction using the total pressure data collected over the period at constant temperature. From this data, a rate constant for the reduction of naphthalene at 2000 psi hydrogen was estimated on the basis of a first-order reaction to be 0.0022 mol/min·g MoS_2 .

The addition of equimolar amounts of each member of the family of inhibitors significantly reduced the rate of naphthalene hydrogenation. For example, addition of an equimolar amount of dibenzothiophene reduced the rate of hydrogenation of naphthalene by a factor of five. Analysis of the recovered products by GC/MS revealed that dibenzothiophene was converted to biphenyl and a mixture of hydrogenated products, including cyclohexylbenzene, tetrahydro-dibenzothiophene and hexahydro-dibenzothiophene. The molar ratio of biphenyl to the total of the hydrogenated products gives the selectivity for the direct HDS pathway versus the hydrogenation pathway for the conversion of DBT. For DBT by itself the value for the ratio HDS/HYD was 0.31. The ratio decreased when naphthalene was added to the reaction mixture, dropping to a value of 0.21 at naphthalene/DBT of 1 and decreasing further to 0.19 at naphthalene/DBT of 2. Thus, naphthalene and DBT are mutually competitive, and naphthalene seems to inhibit the direct HDS function of MoS_2 to a greater degree than the hydrogenation function. Product selectivity over this catalyst for HDS and HYD pathways is a function of feedstock composition.

Other compounds that are structurally related to DBT inhibit the hydrogenation of naphthalene to an even greater degree. The hydrocarbon analog of DBT, fluorene, is much less reactive than naphthalene, yet strongly inhibits the reactions of both naphthalene and DBT. When fluorene is mixed with either naphthalene or DBT, the total rate of hydrogen uptake is greatly reduced and becomes dominated by the rate of the kinetically slow competitor. The same pattern was found when dibenzofuran or carbazole was used as a competitive inhibitor. Both exhibited relatively low activity by themselves, but strongly inhibited hydrogenation of naphthalene. These results illustrate the problematic nature of comparing the activity of different catalysts when they are tested using feedstocks containing more than one reactive component.

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